

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



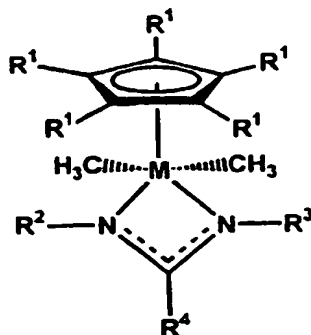
(43) International Publication Date  
3 May 2001 (03.05.2001)

PCT

(10) International Publication Number  
**WO 01/30858 A1**

- (51) International Patent Classification<sup>7</sup>: C08F 4/642 (81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (21) International Application Number: PCT/US00/00328
- (22) International Filing Date: 7 January 2000 (07.01.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/162,037 28 October 1999 (28.10.1999) US
- (71) Applicants and  
(72) Inventors: SITA, Lawrence, R. [US/US]; Apartment 213, 8339 16th Street, Silver Spring, MD 20910 (US). JAYARATNE, Kumudini, C. [LK/US]; Apartment 110, 4800 Berwyn House Road, College Park, MD 20740 (US).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— With international search report.
- (74) Agents: ESMOND, Robert, W. et al.; Sterne, Kessler, Goldstein & Fox P.L.L.C., Suite 600, 1100 New York Avenue, N.W., Washington, DC 20005-3934 (US).
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: STEREOSPECIFIC LIVING POLYMERIZATION OF OLEFINS BY A NOVEL ZIEGLER-NATTA CATALYST COMPOSITION



(I)

(57) Abstract: An olefin polymerization pre-catalyst and a method for preparing an activated olefin polymerization catalyst composition from the pre-catalyst are disclosed in formula (I): wherein M, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are defined herein.

WO 01/30858 A1

**THIS PAGE BLANK (USPTO)**

## **Stereospecific Living Polymerization of Olefins by a Novel Ziegler-Natta Catalyst Composition**

### ***Background of the Invention***

#### ***Field of the Invention***

5           The present invention relates to novel olefin polymerization pre-catalysts which have exhibited the ability to polymerize a variety of  $\alpha$ -olefins in a stereospecific and living fashion when activated by a co-catalyst.

#### ***Related Art***

10           It is well-known that certain aluminum alkyls such as ethylaluminum chlorides form heterogeneous olefin polymerization catalysts in combination with titanium tetrachloride, as is evident from the independent work of Ziegler and Natta. Ziegler, *Angew. Chem.* 67: 213 (1955); Natta *et al.*, *J. Am. Chem. Soc.* 77: 1708 (1955). U.S. Patent No. 2,827,446 to Breslow provides a modified version  
15 of those first generation catalysts wherein triethylaluminum was used as the co-catalyst in place of diethylaluminum chloride.

          Typical Ziegler-Natta catalysts are all heterogeneous systems, which means that complicated surface phenomena strongly influence the catalyst performance. Many attempts have been made to explain and also to modify the performance of  
20 such so-called multiple-site catalysts.

          A very early and important approach was that of Natta and Breslow in which each independently used a soluble transition metal compound/aluminum alkyl system in order to study the mechanism of Ziegler-Natta catalysis in homogeneous media. Natta, *Chem. Ind* 39: 1032 (1957); Breslow *et al.*, *J. Am. Chem. Soc.* 79: 5073 (1957); Breslow *et al.*, *J. Am. Chem. Soc.* 81: 81 (1959).  
25 It was found that the combination of diethylaluminum chloride and titanocene dichloride resulted in an ethylene polymerization catalyst. However, the activity

of this catalyst was found to be much less than the heterogeneous Ziegler-Natta catalysts.

The next milestone of olefin polymerization catalysis was marked by Sinn and Kaminsky, who determined that partly hydrolyzed aluminum alkyls known as aluminoxanes are highly effective co-catalysts for metallocene-type transition metal complexes. In particular, the combination of metallocenes based on zirconium, titanium and hafnium with methyl aluminoxane (MAO) was found to yield much more active polymerization catalysts than the usual heterogeneous Ziegler-Natta catalysts in many olefin polymerization reactions. Sinn *et al.*, *Angew. Chem.* 92: 39 (1980). Sita and Babcock also describe a combination of metallocenes based on titanium with MAO that was found to yield active polymerization catalysts in the polymerization of ethylene, albeit with lower polymerization activity than with known  $d^0$  group 4 metal complexes. Sita *et al.*, *Organometallics*, 17: 5228 (1998).

In addition to their very high polymerization activity, the Kaminsky-Sinn metallocene/methyl aluminoxane catalysts have additional advantageous features which include: (a) access to new polymer modifications in terms of chemical, physical and mechanical properties and (b) access to new polymer structures including specific comonomer incorporation, highly stereoselective polymerization and the reduction of undesirable side-product formation.

Because of these important advantages, metallocene-based "single-site" catalysts have unleashed a technology revolution in industrial olefin polymerization as reflected in the rapidly increasing amount of literature in this field.

Despite the numerous advantages noted above, the particular application of MAO as the co-catalyst for metallocenes introduces some intractable problems with this technology. One such problem is that a considerable excess of methylaluminoxane compared to the amount of metallocene is required in order to get a satisfactory polymerization activity. Typically the transition metal/aluminum molar ratio is between 1:100 and 1:2000. Furthermore, MAO is

readily soluble only in aromatic hydrocarbons, and hence these rather unfavorable solvents must be used in any homogeneous polymerization process.

A further complication in the use of MAO arises from the limited shelf-life of methyl-aluminoxane in aromatic hydrocarbons: aging can cause gel formation in such MAO solutions and thus hinder the preparation of homogeneous catalyst systems.

Because of the importance of single-site catalysts, persistent attempts have been made to overcome the MAO-related problems by modifying MAO through incorporation of higher alkyl groups (i.e. isobutyl groups) or supporting the co-catalyst on silica or other inorganic carriers.

Even if these co-catalysts modifications eventually solve most of the above-mentioned problems, other problems may arise in their turn, namely the reduced polymerization activity of MAO modified through incorporation of higher alkyl groups and the insolubility of supported MAO, which restricts its application to slurry and gas-phase processes.

Another approach has been to find a surrogate for MAO by using ionic complexes based on organoboron compounds as activators. One such boron compound, dimethylanilinium tris(pentafluorophenyl)borate ( $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ ) has been used to convert the metallocene into an active, homogeneous olefin polymerization catalyst. Hlatky *et al.*, *J. Am. Chem. Soc.* 111:2728-2729 (1989). The main advantage of such systems is that high polymerization activity is achieved at a stoichiometric metallocene/activator ratio of 1:1.

U.S. Patent No. 5,812,202 discloses a method for preparing an activated catalyst composition which comprises reacting a "single site" catalyst precursor with an activating co-catalyst (e.g.,  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ ) before, during or after reacting the single site catalyst precursor with a weakly coordinating electron donor such as 1-hexene.

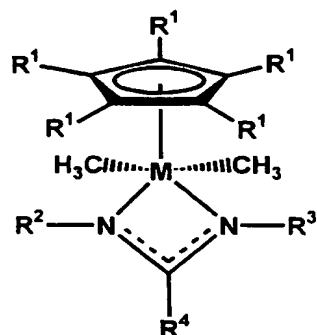
In view of the disadvantages noted in the prior art polymerization catalysts, there is still need for improved, versatile, high-performance olefin polymerization

5 catalysts. In addition, although major advances have been made during the past decade in the development of Ziegler-Natta catalysts that perform either stereospecific (See Brintzinger *et al.*, *Angew. Chem. Int. Ed. Engl.* 34:1143-1170 (1995); Britovsek *et al.*, *Angew. Chem. Int. Ed. Engl.* 38:428-447 (1999); Asanuma *et al.*, *Polym. Bull.* 25:567-570 (1991); Coughlin and Bercaw, *J. Am. Chem. Soc.* 114:7606-7607 (1992); Kesti *et al.*, *J. Am. Chem. Soc.* 114:9679-9680 (1992); Babu *et al.*, *Macromolecules* 27:3383-3388 (1994); van der Linden *et al.*, *J. Am. Chem. Soc.* 117:3008-3021 (1995); Yamaguchi *et al.*, *J. Polym. Sci. A: Polym. Chem.* 37:283-292 (1999); Stehling *et al.*, *Macromolecules* 32:14-20 (1999)) or living polymerization (See Doi *et al.*, *Macromolecules* 19:2896-2900 (1986); Scollard and McConville, *J. Am. Chem. Soc.* 118:10008-10009 (1996); Baumann *et al.*, *J. Am. Chem. Soc.* 119:3830-3831 (1997); Killian *et al.*, *J. Am. Chem. Soc.* 118:11664-11665 (1996); Hagihara *et al.*, *Macromolecules* 31:3184-3188 (1998); Yasuda *et al.*, *J. Am. Chem. Soc.* 114:4908-4910 (1992)) of  $\alpha$ -olefins, there is still a complete lack of highly active homogeneous catalysts that can effect both simultaneously. The present invention relates to a class of transition metal complexes that function as catalyst precursors for the living Ziegler-Natta polymerization of  $\alpha$ -olefins upon activation by a borate co-catalyst. More importantly, these transition metal complexes possess the ability to polymerize  $\alpha$ -olefins in *both* a stereospecific *and* living fashion.

### *Summary of the Invention*

The invention relates to an olefin polymerization pre-catalyst of the Formula (I) and a method for preparing an activated olefin polymerization catalyst composition, which comprises reacting an olefin polymerization pre-catalyst having the Formula (I):

-5-



wherein the dotted lines indicate a delocalized bond;

each  $R^1$  is independently hydrogen or alkyl or two adjacent  $R^1$  form an aromatic ring;

5 each  $R^2$ ,  $R^3$  and  $R^4$  are independently alkyl, cycloalkyl, phenyl or an optionally substituted phenyl; and

M is Zr or Hf;

with an activating co-catalyst having the Formula:



10 wherein  $A^+$  is a cationic Lewis or Brønsted acid capable of abstracting a methyl from the metal, M, of the olefin polymerization pre-catalyst;

B is the element boron; and

$R^5$  is phenyl or an optionally substituted phenyl.

15 The invention further relates to an activated olefin polymerization catalyst composition obtained by the method of the present invention.

The invention further relates to a method for preparing a polyolefin, comprising reacting an  $\alpha$ -olefin with the activated olefin polymerization catalyst composition of the present invention under conditions whereby the polyolefin is produced.

20 The invention further relates to the method for preparing a polyolefin, comprising reacting a diene with the activated olefin polymerization catalyst

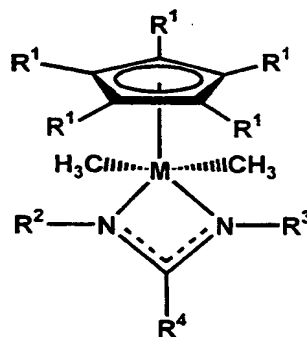
composition of the present invention under conditions whereby the polyolefin is produced.

The invention further relates to the method for preparing a block co-polymer, comprising reacting a combination of two or more different  $\alpha$ -olefins, two or more different dienes or two or more different aromatic compounds having vinyl unsaturation or any combination thereof, with the activated olefin polymerization catalyst composition of the present invention under conditions whereby said block co-polymer is produced.

The invention further relates to the polyolefin or block co-polymer obtained by the method of present invention.

The invention further relates to the method for preparing a highly isotactic polyolefin or block co-polymer, comprising:

- (a) preparing an activated olefin polymerization catalyst, which comprises reacting an olefin polymerization pre-catalyst having the Formula (I):



wherein the dotted lines indicate a delocalized bond;

each  $R^1$  is independently hydrogen or alkyl or two adjacent  $R^1$  form an aromatic ring;

each  $R^2$ ,  $R^3$  and  $R^4$  are independently alkyl, cycloalkyl, phenyl or an optionally substituted phenyl;

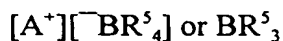
with the proviso that  $R^2$  and  $R^3$  are not the same; and

M is Zr, Ti or Hf;



-7-

with an activating co-catalyst having the Formula:



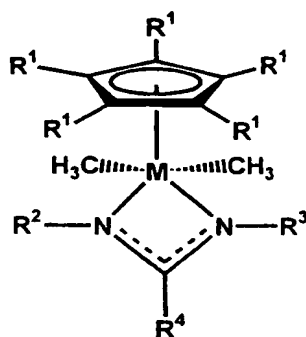
wherein  $A^+$  is a cationic Lewis or Brønsted acid capable of abstracting a methyl from the metal, M, of the olefin polymerization pre-catalyst;

B is the element boron; and

$R^5$  is phenyl or an optionally substituted phenyl; and

(b) reacting an  $\alpha$ -olefin or a combination of two or more unlike  $\alpha$ -olefins with the activated olefin polymerization catalyst under conditions whereby said highly isotactic polyolefin or block-copolymer is produced.

The invention further relates to the olefin polymerization pre-catalyst of Formula (I):



wherein the dotted lines indicate a delocalized bond;

M is Zr or Hf;

each  $R^1$  is independently hydrogen or alkyl or two adjacent  $R^1$  form an aromatic ring;

each  $R^2$ ,  $R^3$  and  $R^4$  are independently alkyl, cycloalkyl, phenyl or an optionally substituted phenyl;

with the proviso that  $R^2$  and  $R^3$  are not the same.

### *Description of the Drawings*

Fig. 1A shows a  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) spectrum for poly(1-hexene) produced from **1** (See Example 1)/ $[\text{B}(\text{C}_6\text{F}_5)_4]$  at  $0^\circ\text{C}$  in chlorobenzene ( $M_n = 11,032$ ;  $M_w/M_n = 1.10$ ).

Fig. 1B shows a  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) spectrum ( $\delta$  40.19, 34.57, 32.33, 28.69, 23.22, 14.19) for poly(1-hexene) produced from **1**/ $[\text{B}(\text{C}_6\text{F}_5)_4]$  at  $-10^\circ\text{C}$  in chlorobenzene ( $M_n=49,251$ ;  $M_w/M_n=1.05$ ). The small resonance marked by the asterisk is tentatively assigned to the mmmr pentad ( $\Delta\delta$  from mmmm) = -0.21 ppm).

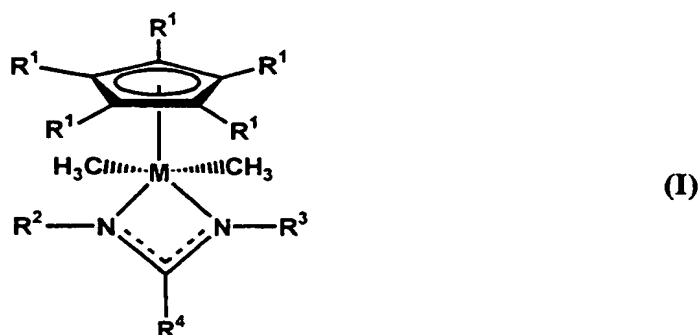
Fig. 2 shows a plot of  $M_n$  versus percent conversion of 1-hexene (initial conditions: 1.97 M in 1-hexene; 50  $\mu\text{mol}$  each of **1** and  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  in chlorobenzene,  $-10^\circ\text{C}$ ; total reaction volume, 10 ml) ( $M_w/M_n = 1.03$ -1.09 for each data point). The dashed line is a linear curve fit of the data. The inset shows a plot of the percent conversion of 1-hexene vs. time where the dashed line is a guide for the eye.

### *Detailed Description of the Preferred Embodiments*

The present invention relates to a novel olefin polymerization pre-catalyst that is converted to an activated olefin polymerization catalyst upon exposure to an activating co-catalyst. The activated olefin polymerization catalyst promotes the stereospecific living polymerization of  $\alpha$ -olefins to provide highly isotactic, high molecular weight materials possessing low polydispersities. The olefin polymerization pre-catalyst may be obtained from an olefin polymerization catalyst precursor.

A preferred olefin polymerization catalyst precursor is the trialkyl metallocene (1,2,3,4,5-tetramethyl)cyclopentadienyl trimethyl zirconium. This metallocene may be converted into an olefin polymerization pre-catalyst via reaction with a symmetric or unsymmetric carbodiimide. When this metallocene

is used,  $R^4$  (*vide infra*) will always be methyl. However, it is known in the art that other olefin polymerization catalyst precursors may be used which elicit the formation of an olefin polymerization pre-catalyst in which  $R^4$  may be other than methyl. See Chernega *et al.*, *J. Chem. Soc. Chem. Commun.*: 1415 (1993). The olefin polymerization pre-catalyst that results from reaction with a unsymmetric carbodiimide is racemic. A preferred olefin polymerization pre-catalyst that results from the reaction of the metallocene with a symmetric (i.e.,  $R_2 = R_3$ ) or unsymmetric (i.e.,  $R_2 \neq R_3$ ) carbodiimide has the Formula (I):



wherein the dotted lines indicate a delocalized bond;

M is Ti, Zr or Hf;

each  $R^1$  is independently hydrogen or alkyl or two adjacent  $R^1$  form an aromatic ring;

each  $R^2$ ,  $R^3$  and  $R^4$  are independently alkyl, cycloalkyl, phenyl or an optionally substituted phenyl.

As used herein, "alkyl" refers to straight- or branched-chain hydrocarbons having from 1 to 10 carbon atoms and more preferably 1 to 8 carbon atoms, including by way of example methyl, ethyl, propyl, *i*-propyl and *t*-butyl.

"Cycloalkyl" refers to cyclic alkyl groups containing between 3 and 8 carbon atoms having a single cyclic ring including, by way of example, cyclopropyl, cyclobutyl, cyclopentyl, cyclooctyl and the like.

"Optionally substituted phenyl" refers to a phenyl ring which may contain 1 to 5 electron donating or electron withdrawing groups. By way of example,

electron donating groups include, but are not limited to amino, hydroxy, alkoxy, N-amide, aryl and alkyl. Examples of electron withdrawing groups include, but are not limited to, halo, ketone, ester,  $-\text{SO}_3\text{H}$ , aldehyde, carboxylic acid, cyano, nitro and ammonium.

5 "Halo" refers to fluoro, chloro, bromo and iodo.

"Aromatic ring" refers to an unsaturated carbocyclic group of 6 to 14 carbon atoms having a single ring (e.g., phenyl) or multiple condensed rings (e.g., naphthyl or anthryl).

10 The olefin polymerization pre-catalyst of the present invention may be prepared using any suitable olefin polymerization catalyst precursor. The olefin polymerization catalyst precursor may be made by any means available; the method of synthesis of the olefin polymerization catalyst precursor is not critical to the invention.

15 The olefin polymerization pre-catalyst of the present invention is converted to an activated olefin polymerization catalyst by using an activating co-catalyst. The activated olefin polymerization catalyst of the present invention thus produced is useful in the polymerization of a variety of  $\alpha$ -olefins in a stereospecific and living fashion. For example, 1-hexene and vinylcyclohexane are polymerized by an activated olefin polymerization catalyst of the present invention to give a highly isotactic and high molecular weight material. In addition, the same catalyst  
20 polymerizes 1-hexene and vinylcyclohexane in a living fashion. Other  $\alpha$ -olefins that may be polymerized with a catalyst of the present invention include, but are not limited to  $\gamma$ -substituted alpha olefins such as 3-methylbutene, 3-methyl-1-pentene, vinylcyclohexene, vinylcyclobutane, vinylcyclopentane, vinylcyclooctane,  
25 1-decene and enantiomerically pure  $\beta$ -citronellene.

The activating co-catalyst is capable of generating the activated olefin polymerization catalyst. Preferably, the activating co-catalyst is one of the following: (a) ionic salts of the general formula  $[\text{A}^+][\text{BR}_4^-]$ , wherein  $\text{A}^+$  is a cationic Lewis or Brønsted acid capable of abstracting a methyl from the olefin

polymerization pre-catalyst, B is the element boron, and R<sup>5</sup> is phenyl or an optionally substituted phenyl or (b) a boron alkyl of the general formula BR<sup>5</sup><sub>3</sub>.

Examples of Lewis or Brønsted acids that may be used in the practice of the invention include, but are not limited to tri-*n*-butylammonium, triphenylcarbonium and dimethylanilinium cations.

The mole ratio of olefin polymerization pre-catalyst to activating co-catalyst usefully employed in the olefin polymerization catalyst composition may vary. When the activating co-catalyst is an ionic salt of the formula [A<sup>+</sup>][<sup>-</sup>BR<sup>5</sup><sub>4</sub>], or a boron alkyl of the formula BR<sup>5</sup><sub>3</sub>, the mole ratio of boron atoms contained in the ionic salt or the boron alkyl to total metal atoms contained in the olefin polymerization pre-catalyst is generally in the range of from about 0.9:1 to about 1.5:1, preferably in the range of from about 1:1 to about 1.1:1.

Reaction of the olefin polymerization pre-catalyst with the activating co-catalyst may typically take place within about 10 seconds to about 30 minutes, most preferably within about 1 to about 10 minutes, at temperatures of about -35 to about 25 °C, preferably about -10 to about 0 °C.

Particularly preferred is an olefin polymerization catalyst composition that is in unsupported, liquid form. For example, the polymerization catalyst composition may be introduced into the reaction zone in unsupported, liquid form as described in U.S. Patent No. 5,317,036. As used herein, "unsupported, liquid form" includes liquid olefin polymerization pre-catalyst, liquid co-catalyst, solution(s) or dispersions thereof in the same or different solvent(s) (e.g., chlorobenzene, isopentane, hexane, toluene, or the like), and combinations thereof. Unsupported, liquid form catalyst compositions have a number of practical benefits. Unsupported catalyst compositions avoid the costs associated with support material and its preparation, and provide for the realization of a very high catalyst surface area to volume ratio. Furthermore, unsupported catalyst compositions produce polymers having a much lower residual ash content than polymers produced using supported catalyst compositions.

The liquid reaction medium may consist of the bulk liquid monomer or an inert liquid hydrocarbon that is nonreactive under the polymerization conditions employed. Although such an inert liquid hydrocarbon need not function as a solvent for the catalyst composition or the polymer obtained by the process, it usually serves as solvent for the monomers employed in the polymerization. Among the inert liquid hydrocarbons suitable for this purpose are chlorobenzene, dichlorobenzene, isopentane, hexane, cyclohexane, heptane, benzene, toluene, trifluorotoluene, pentane, octane, isooctane, dichloromethane and the like. Reactive contact between the olefin monomer and the catalyst composition should be maintained by constant stirring or agitation. The reaction medium containing the olefin polymer product and unreacted olefin monomer may be withdrawn from the reactor continuously. The olefin polymer product may be separated, and the unreacted olefin monomer and liquid reaction medium may be recycled into the reactor.

U.S. Patent No. 5,912,202 teaches that polymerization may be carried out in a single reactor or in two or more reactors in series, and is conducted substantially in the absence of catalyst poisons. According to U.S. Patent No. 5,681,908 catalyst poisons may include water, oxygen, carbon dioxide, hydrogen, sulfur and acetylene. U.S. Patent No. 5,674,795 teaches that even minor amounts (i.e.,  $\leq 2$  ppm) of such materials have been found to affect the polymerization adversely. According to the present invention, organometallic compounds may be employed as scavenging agents for poisons and to increase the catalyst activity. Examples of scavenging agents are metal alkyls, preferably aluminum alkyls, most preferably triisobutylaluminum.

Conventional adjuvants may be included in the process, provided they do not interfere with the operation of the activated olefin polymerization catalyst composition in forming the desired polyolefin. Hydrogen or a metal or non-metal hydride, e.g., a silyl hydride, may be used as a chain transfer agent in the process.

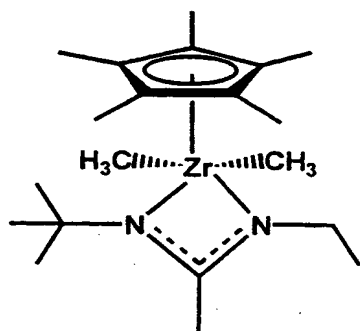
Polyolefins that may be produced according to the invention include, but are not limited to, those made from olefin monomers such as ethylene and linear

or branched higher  $\alpha$ -olefin monomers containing 3 to about 20 carbon atoms. Homopolymers or block-copolymers of ethylene and such higher alpha-olefin monomers, with densities ranging from about 0.86 to about 0.95 may be made. In addition, homopolymers and block-copolymers that have high isotacticity and low polydispersities may be made. For example, high isotacticity, as determined using the pentad level of analysis, is from about 90 to 100 percent, preferably from about 97 to 100 percent. *See Asakura et al., Macromolecules 24:2334-2340 (1991).* Low polydispersity is, for example, from about 1.01 to 2.0. Suitable higher alpha-olefin monomers include, for example, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 3,5,5-trimethyl-1-hexene, vinylcyclohexane, 3-methylbutene, 3-methyl-1-pentene, vinylcyclobutane, vinylcyclopentane, vinylcyclooctane, 1-decene and enantiomerically pure  $\beta$ -citronellene. Olefin polymers according to the invention may also be based on or contain conjugated or non-conjugated dienes, such as linear, branched, or cyclic hydrocarbon dienes having from about 4 to about 20, preferably 4 to 12, carbon atoms. Preferred dienes include 1,4-pentadiene, 1,5-hexadiene, 5-vinyl-2-norbornene, 1,7-octadiene, vinylcyclohexene, dicyclopentadiene, butadiene, isobutylene, isoprene, ethylidene norbornene and the like. Aromatic compounds having vinyl unsaturation such as styrene and substituted styrenes, vinyl trialkyl silanes and the like may be polymerized according to the invention as well. Specific polyolefins that may be made according to the invention include, for example, poly-1-hexene, polyvinylcyclohexane, 1-hexene/vinylcyclohexane block co-polymers, polyethylene, polypropylene, ethylene/propylene rubbers (EPR's), ethylene/propylene/diene terpolymers (EPDM's), polybutadiene, polyisoprene and the like, as well as a variety of di- and ter-block co-polymers.

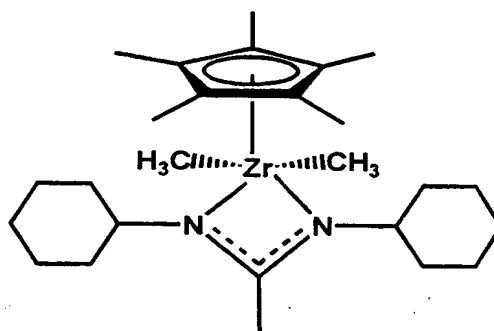
Having now generally described this invention, the same will be understood by reference to the following examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

### Example 1

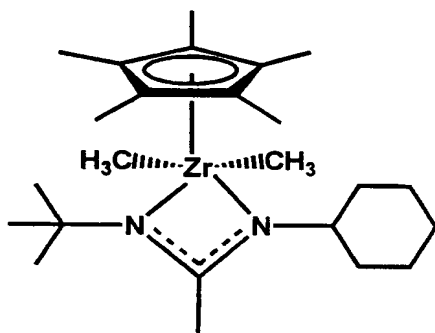
#### Synthesis and Evaluation of Activated Olefin Polymerization Catalysts 1 & 2



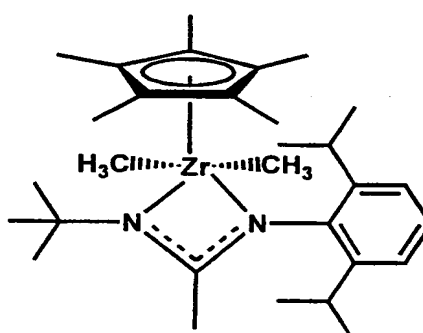
1



2



3



4

Dry, oxygen-free solvents and standard Schlenk line and glovebox techniques were used throughout. Chlorobenzene was distilled from calcium hydride. Pentane, diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl. 1-hexene (>99%, Aldrich) was distilled from sodium/potassium alloy. GC analysis of the 1-hexene confirmed that its isomeric purity was greater than 99%. Dicyclohexylcarbodiimide, 1-*t*-butyl, 3-ethylcarbodiimide and [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Strem) were obtained from commercial sources and used as obtained.



**A. Synthesis of Olefin Polymerization Pre-catalyst 1.**

To a solution of 0.5g (1.84 mmol) of  $\text{Cp}^*\text{ZrMe}_3$  ( $\text{Cp}^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl anion) in 10 ml of pentane, a solution of 0.23 g (1.84 mmol) of 1-*t*-butyl, 3-ethylcarbodiimide in 10 ml of pentane was added and the mixture stirred at room temperature for 18 h. Upon removal of the volatiles *in vacuo*, the crude material was recrystallized from pentane at  $-35^\circ\text{C}$  to provide the desired compound 1 in a 71% yield as a white crystalline material. For 1:  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ )  $\delta$  0.23 (s, 6H), 0.90 (t, 3H,  $J = 7.2$  Hz), 1.16 (s, 9H), 1.70 (s, 3H), 2.01 (s, 15H), 2.86 (q, 2H,  $J = 7.2$  Hz). Anal. Calcd. for  $\text{C}_{20}\text{H}_{38}\text{N}_2\text{Zr}$ : C, 60.39; H, 9.63; N, 7.04. Found: C, 60.54; H, 9.61; N, 7.03.

**B. Synthesis of Olefin Polymerization Pre-catalyst 2.**

Compound 2 was prepared in a similar fashion. For 2 (68% yield):  $^1\text{H}$  NMR (400 MHz, benzene- $d_6$ )  $\delta$  0.34 (s, 6H), 1.11 (m, 6H), 1.48 (m, 6H), 1.68 (s, 3H), 1.73 (m, 8H), 2.04 (s, 15H), 2.95 (tt, 2H,  $J = 3.6$  Hz,  $J = 11.5$  Hz). Anal. Calcd. for  $\text{C}_{26}\text{H}_{46}\text{N}_2\text{Zr}$ : C, 65.35; H, 9.70; N, 5.86. Found: C, 64.97; H, 9.67; N, 6.02.

**C. General Polymerization Procedure (either 2 M or 32 M in 1-hexene).**

The activated olefin polymerization catalyst was prepared by adding a solution of 25  $\mu\text{mol}$  of either 1 or 2 in 4 ml of chlorobenzene, precooled to  $-35^\circ\text{C}$ , to a solution of 25  $\mu\text{mol}$  of  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  in 4 ml of chlorobenzene also precooled to  $-35^\circ\text{C}$ . After 10 min at  $-35^\circ\text{C}$ , the bright yellow activated olefin polymerization catalyst solution was brought to the polymerization temperature whereupon 2 ml of 1-hexene, precooled to the polymerization temperature, was added rapidly and all at once via cannula. At the desired time, the polymerization was quenched by the addition of acidified (HCl) methanol and the volatiles removed *in vacuo* ( $\sim 0.01$  mm Hg). Purification of the polymer was achieved by precipitation of a toluene solution into a large volume of methanol, collecting the solid material and drying it overnight at  $60^\circ\text{C}$  / 0.01 mm Hg. The yields and GPC analyses of the purified polymers revealed no significant changes

from those of the crude materials. For polymerizations that are 32 M in 1-hexene, the catalyst was prepared in only 2 ml of chlorobenzene in the same fashion as above, and then 8 ml of 1-hexene, precooled to the polymerization temperature, was added all at once.

5 For kinetic analysis of the polymerizations, a weighed amount of undecane was used as an internal standard. Aliquots were then drawn at measured time intervals and the percent conversion of the monomer determined by GC analysis.

#### D. Polymer Characterization

10 GPC analyses were performed using a Waters GPC system equipped with a column oven and differential refractometer both maintained at 35° C and four columns (Waters Ultrastyrigel 500Å, Waters Styragel HR3, Waters Styragel HR4 and Shodex K-806M) also maintained at 35° C. THF was used as the eluant at a flow rate of 1.1 ml/min.  $M_n$  and  $M_w/M_n$  values were obtained using the Waters GPC software and seven different polystyrene standards (Polymer Laboratories).

#### 15 E. Evaluation of Olefin Polymerization Pre-catalysts 1 and 2

Prior studies with compounds closely related to 1-4 have provided only disappointing results with respect to the Ziegler-Natta polymerization of either ethene or propene. Sita and Babcock, *Organometallics* 17:5228-5230 (1998); Buijink *et al.*, *Naturforsch.* 46B:1328-1332 (1991); Chernega *et al.*, *J. Chem. Soc., Chem. Commun.*:1415-1417 (1993); Gomez *et al.*, *J. Chem. Soc., Chem. Commun.*:2607-2608 (1994); Gomez *et al.*, *J. Organometal. Chem.* 491:153-158 (1995). As Table 1 shows, however, upon activation with the borate, [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], compound 2 surprisingly proved to be capable of functioning as a competent activated olefin polymerization catalyst for the polymerization of 1-hexene at 0° C in chlorobenzene. Importantly, the narrow polydispersity (monomodal,  $M_w/M_n$  = 1.10), and the lack of olefinic resonances in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the poly(1-hexene) formed, strongly suggested a living character for this polymerization process that is devoid of termination via β-hydride elimination. Babu *et al.*, *Macromolecules* 27:3383-3388 (1994). However, as Fig. 1A reveals, the <sup>13</sup>C NMR spectrum of this material also

20

25

30

clearly pointed to a lack of stereocontrol of polymer microstructure with this particular system. Babu *et al.*, *Macromolecules* 27:3383-3388 (1994); Asakura *et al.*, *Macromolecules* 24:2334-2340 (1991).

Given the promising results with 2, and those of Ewen and co-workers who were able to produce highly isotactic polypropylene from the chiral  $C_1$  symmetric metallocene,  $\text{Me}_2\text{C}(3\text{-}t\text{-Bu-C}_5\text{H}_3)(9\text{-fluorenyl})\text{ZrCl}_2$ , it was of interest to determine if the racemic compounds 1, 3 and 4, could serve in a similar capacity. Ewen, *J. Mol. Catal. A: Chem.* 128:103-109 and references cited therein (1998). In this regard, while compounds 3 and 4 exhibited dramatically reduced activity, with only oligomers being produced under identical conditions as a possible result of too much steric hindrance imposed by these particular acetamidinate substituents, 1 proved to be an exceptional olefin polymerization pre-catalyst for the polymerization of 1-hexene with respect to providing both a higher activity and a higher molecular weight for the poly(1-hexene) formed when the process was started at room temperature (see Table 1, entry 1). Inspection of the  $^{13}\text{C}$  NMR spectrum for this material also revealed it to be highly isotactic (mmmm>95%). Indeed, the only indication that these conditions were potentially non-ideal for both the stereospecific, and living, polymerization of 1-hexene was provided by the broader polydispersity index ( $M_w/M_n$ ) of 1.50 that was obtained for this poly(1-hexene). However, when the polymerization was performed with 1 at lower temperature, both an increase in the molecular weights and a decrease in the polydispersities of the poly(1-hexene)s produced was observed while the relatively high activities were maintained (Table 1, entries 2 and 3). Most significantly, the high molecular weight poly(1-hexene) obtained at  $-10^\circ\text{C}$  had a polydispersity of only 1.03, thereby indicating that this polymerization was living. As the  $^{13}\text{C}$  NMR spectrum shown in Fig. 1B reveals the polymerization was stereospecific for the formation of isotactic material (mmmm>95%). Additional proof for the living character of the polymerization of 1-hexene conducted under these last conditions was provided by a plot of the number-average molecular weight,  $M_n$ , of the poly(1-hexene) produced vs. the extent of monomer consumed

which yielded a linear correlation as shown in Fig. 2. Finally, it was shown by one polymerization experiment (initial conditions: 180 equiv. of 1-hexene; 50  $\mu$ mol of activated **1** in chlorobenzene, -10°C, total reaction volume, 10 ml) that the polymer formed ( $M_n$ =20,732,  $M_w/M_n$ =1.03) after complete consumption of the monomer ( $t$ =60 min) was still living by the formation of a higher molecular weight polymer ( $M_n$ =35,372,  $M_w/M_n$ =1.13) upon introduction of another 180 equiv. of 1-hexene and carrying out the polymerization for an additional 40 min.

**Table 1:** 1-Hexene Polymerization Data.

Entry	Pre-catalyst <sup>a</sup>	[H] <sup>b</sup> (M)	Temp. (°C)	Time (min)	Activity <sup>c</sup>	$M_n^d$	$M_w/M_n$
1	1	32	25 <sup>a</sup>	15	110	32,572	1.50
2	"	2	0	15	76	43,544	1.23
3	"	2	-10	15	64	49,251	1.03
4	"	"	"	30	N/A	69,544	1.10
5	2	32	0	30	9	11,032	1.10

<sup>a</sup> Prepared from equimolar (25  $\mu$ mol) amounts of the zirconium complex (i.e., olefin polymerization pre-catalyst) and [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in chlorobenzene; total reaction volume, 10 ml.

<sup>b</sup> [H] = [1-hexene]

<sup>c</sup> g<sub>polymer</sub>•mmol<sub>cat</sub><sup>-1</sup>•h<sup>-1</sup>

<sup>d</sup> Determined by GPC analysis at 35°C using polystyrene standards and THF as the eluant.

<sup>e</sup> Exotherm observed for polymerization initiated at this temperature.

## Example 2

### *Polymerization of Vinylcyclohexane to Give Isotactic Polyvinylcyclohexane (iso-PVCH)*

The activated olefin polymerization catalyst was prepared in a glove box by adding a solution of 25  $\mu$ mol (10mg) of compound **1** in 1 ml of chlorobenzene, precooled to -35° C, to a solution of 25  $\mu$ mol (20mg) of [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

in 1 ml of chlorobenzene, also precooled to  $-35^{\circ}\text{C}$ . 8 ml of vinylcyclohexane was then added to the yellow activated olefin polymerization catalyst solution at room temperature and the resulting mixture stirred for 15 min, after which time, the polymerization was quenched by the addition of methanol and the volatiles removed in *vacuo* (0.01 mm Hg). The solid material was dried overnight at  $100^{\circ}\text{C}$  / 0.01 mm Hg to yield 0.37 g of the polymer (activity:  $60 \text{ kg}_{\text{polymer}} \text{ mol}_{\text{cat}}^{-1} \text{ h}^{-1}$ ).

### *Example 3*

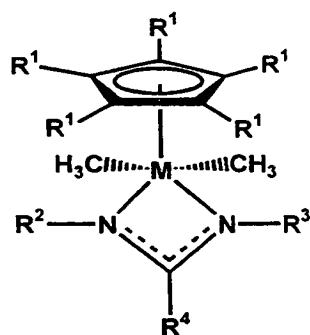
#### *Polymerization of Vinylcyclohexane and 1-Hexene to Give an Isotactic Block Co-Polymer*

The activated olefin polymerization catalyst was prepared in a glove box by adding a solution of 25  $\mu\text{mol}$  (10 mg) of compound 1 in 2.22 ml of chlorobenzene, precooled to  $-10^{\circ}\text{C}$ , to a solution of 25 mmol (20 mg) of  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  in 2.22 ml of chlorobenzene also precooled to  $-10^{\circ}\text{C}$ . 0.56 ml (0.38 g) of 1-hexene, which was precooled to  $-10^{\circ}\text{C}$ , was added to the yellow activated olefin polymerization catalyst solution and the reaction was stirred for 1 h at  $-10^{\circ}\text{C}$ . After 1 h, 6 ml of vinylcyclohexane was added all at once to the reaction mixture which was then warmed to room temperature and stirred for 1 h. The polymerization was then quenched by the addition of methanol and the volatiles removed in *vacuo* (0.01 mm Hg). The solid material was dried overnight at  $100^{\circ}\text{C}$  / 0.01 mm Hg to yield 1.2 g of the polymer.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions without undue experimentation. All patents, patent applications and publications cited herein are incorporated by reference in their entirety.

***What Is Claimed Is:***

1. A method for preparing an activated olefin polymerization catalyst composition, which comprises reacting an olefin polymerization pre-catalyst having the formula:



wherein the dotted lines indicate a delocalized bond;

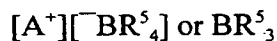
each R¹ is independently hydrogen or alkyl or two adjacent R¹ form an aromatic ring;

each R², R³ and R⁴ are independently alkyl, cycloalkyl, phenyl or an optionally substituted phenyl;

with the proviso that R² and R³ are not the same; and

M is Zr or Hf;

with an activating co-catalyst having the formula:



wherein A⁺ is a cationic Lewis or Brønsted acid capable of abstracting a methyl from the metal, M, of the olefin polymerization pre-catalyst;

B is the element boron; and

R⁵ is phenyl or an optionally substituted phenyl.

-21-

2. The method of claim 1 wherein M is Zr.

3. The method of claim 1 wherein the activating co-catalyst is  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ .

4. The method of claim 1 wherein the olefin polymerization pre-catalyst is (1,2,3,4,5-pentamethyl)cyclopentadienyl dimethyl zirconium (N-*t*-butyl-N-ethyl)amidinate.

5. An activated olefin polymerization catalyst composition obtained according to the method of claim 1.

6. A method for preparing a polyolefin, comprising reacting an  $\alpha$ -olefin with the activated olefin polymerization catalyst composition of claim 5 under conditions whereby said polyolefin is produced.

7. A method for preparing a polyolefin, comprising reacting a diene with the activated olefin polymerization catalyst composition of claim 5 under conditions whereby said polyolefin is produced.

8. A method for preparing a polyolefin, comprising reacting an aromatic compound having vinyl unsaturation with the activated olefin polymerization catalyst composition of claim 5 under conditions whereby said polyolefin is produced.

9. A method for preparing a block co-polymer, comprising reacting a combination of two or more different  $\alpha$ -olefins, two or more different dienes or two or more different aromatic compounds having vinyl unsaturation or any combination thereof, with the activated olefin polymerization catalyst composition of claim 5 under conditions whereby said block co-polymer is produced.

10. The polyolefin or block co-polymer obtained by the method of claims 6, 7, 8 or 9.

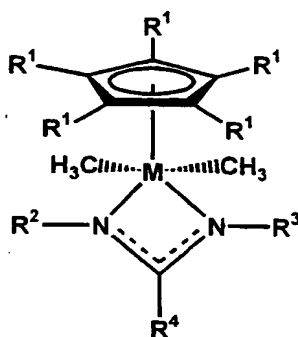
11. The polyolefin or block co-polymer of claim 10, wherein said polyolefin or block co-polymer is highly isotactic.

12. The polyolefin or block-copolymer of claim 11, wherein said polyolefin or block co-polymer has a low polydispersity.

13. The method of claims 6, 7, 8 or 9, wherein said polyolefin or block co-polymer is produced in a living fashion.

14. A method for preparing a highly isotactic polyolefin or block co-polymer, comprising:

(a) preparing an activated olefin polymerization catalyst, which comprises reacting an olefin polymerization pre-catalyst having the formula:



wherein the dotted lines indicate a delocalized bond;  
each R¹ is independently hydrogen or alkyl or two adjacent R¹ form an aromatic ring;

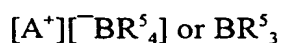


each  $R^2$ ,  $R^3$  and  $R^4$  are independently alkyl, cycloalkyl, phenyl or an optionally substituted phenyl;

with the proviso that  $R^2$  and  $R^3$  are not the same; and

M is Zr, Ti or Hf;

5 with an activating co-catalyst having the formula:



wherein  $A^+$  is a cationic Lewis or Brønsted acid capable of abstracting a methyl from the metal, M, of the olefin polymerization pre-catalyst;

B is the element boron; and

10  $R^5$  is phenyl or an optionally substituted phenyl; and

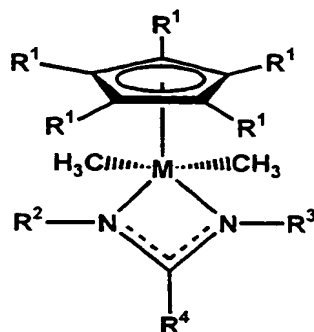
(b) reacting an  $\alpha$ -olefin or a combination of two or more unlike  $\alpha$ -olefins with the activated olefin polymerization catalyst under conditions whereby said highly isotactic polyolefin or block-copolymer is produced.

15 15. The method of claim 14, wherein said polyolefin or block copolymer is produced in a living fashion.

16. The method of claim 14, wherein said polyolefin or block copolymer has a low polydispersity.

17. An olefin polymerization pre-catalyst of the formula:

-24-



wherein the dotted lines indicate a delocalized bond;

M is Zr or Hf;

each R<sup>1</sup> is independently hydrogen or alkyl or two adjacent R<sup>1</sup> form an aromatic ring;

each R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently alkyl, cycloalkyl, phenyl or an optionally substituted phenyl;

with the proviso that R<sup>2</sup> and R<sup>3</sup> are not the same.

1/2

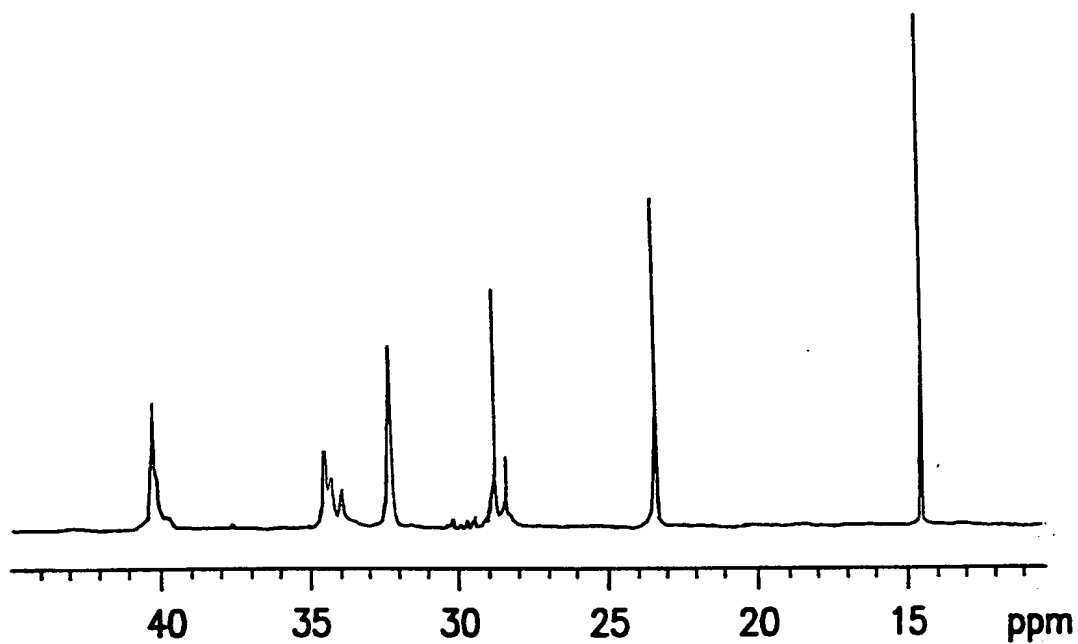


FIG. 1A

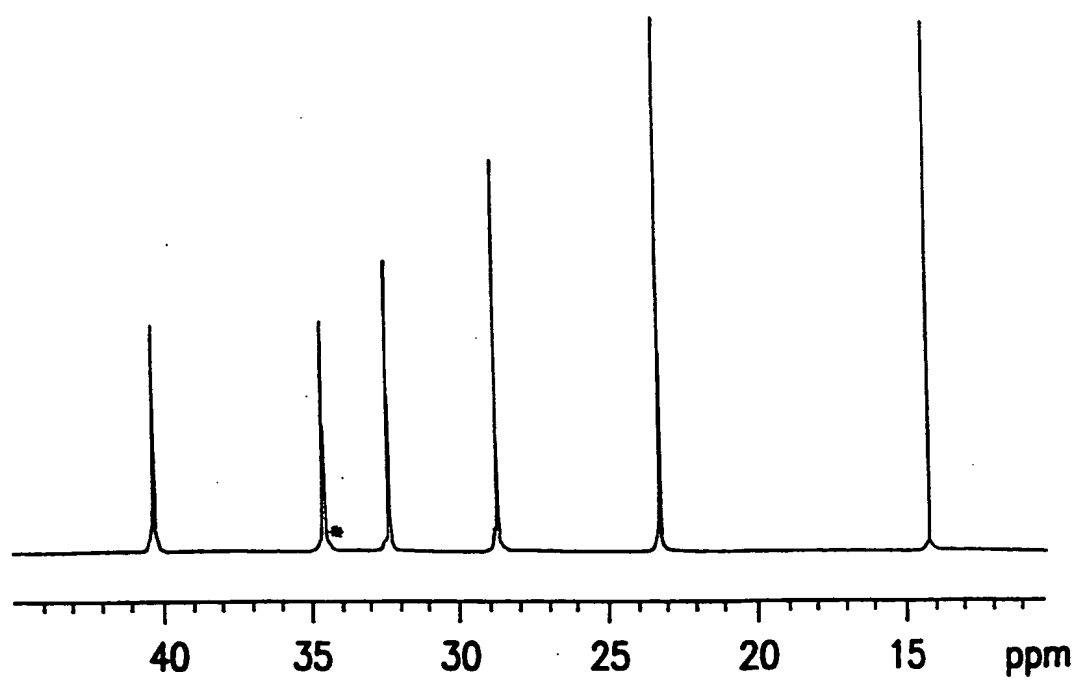


FIG. 1B

**THIS PAGE BLANK (USPTO)**

2/2

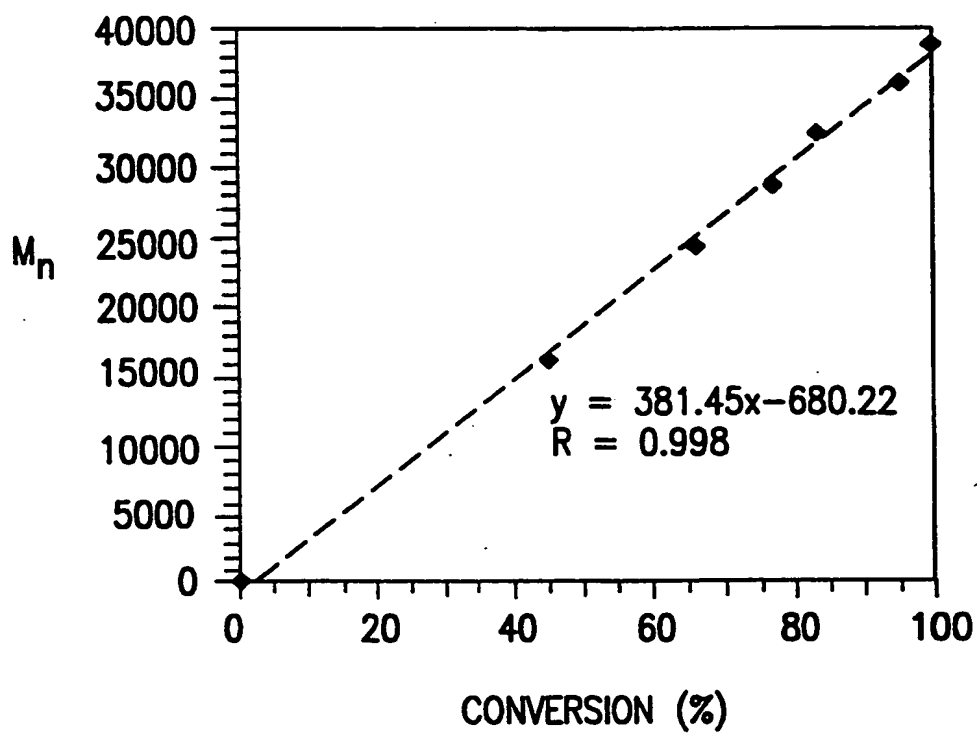


FIG.2A

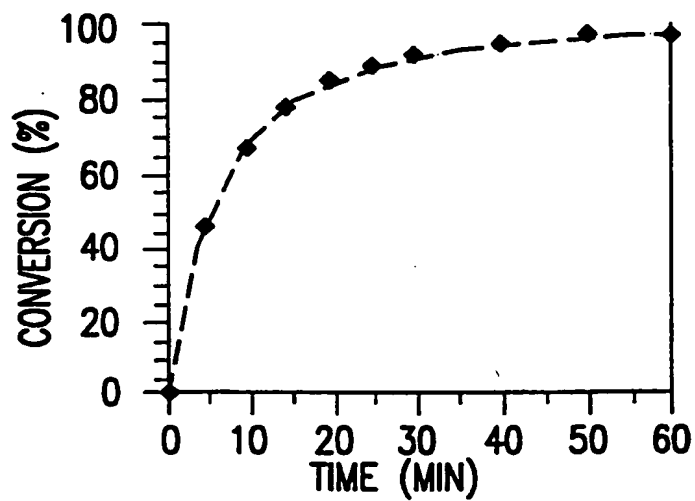


FIG.2B

**THIS PAGE BLANK (USPTO)**

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/00328

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C08F 4/642

US CL : 502/104, 117, 152, 155; 526/134, 170

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/104, 117, 152, 155; 526/134, 170

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 1.2

search terms: bridged bis(amido), cyclopentadienyl, zirconium or hafnium, olefin

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,527,752 A [REICHLE et al] 18 June 1996, col. 2, lines 45-67; col. 3, lines 1-16; col. 6, line 28; col. 8, lines 37-58.	1-17
A	US 5,318,935 A [CANICH et al] 07 June, 1994, col.13, lines31-68; col. 14, lines 1-3; col. 10, lines 10-17.	1-17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

14 MARCH 2000

Date of mailing of the international search report

11 APR 2000

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

LING-SIU CHOI

Telephone No. (703) 308-0661

**THIS PAGE BLANK (USPTO)**